Environmentally Friendly Cleaners for Removing Tar and Asphalt from Tactical and Transportation Vehicles

Veera M. Boddu (Speaker), Joyce C. Baird, Qi Chen, and Chris Myers
US Army Engineer Research & Development Center (ERDC-CERL)
Champaign, IL 61822

Pam Khabra
TACOM/TARDEC, Warren, MI 48397

Wayne Ziegler
Army Research Laboratories (ARL/WMRD) Bldg 4600, APG, MD 21005

Malcolm E. McLeod
US Army Corps of Engineers, Public Works Department, Washington, DC 20314

Veera.Boddu@usace.army.mil

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Presentation Outline

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  - Problem
- **Objective**
  - Environmentally Friendly Cleaners for Tar/Asphalt Removal
- **Approach**
  - Criteria for Solvent Selection
  - Literature Review
  - Laboratory Evaluation
    - Coupon studies
    - Field sample cleaning
- **Results and Analysis**
- **Conclusions and Recommendations**

BACKGROUND

- Cleaning the road tar/asphalt is a standard practice prior to induction of a vehicle back in to service.
- Current practice is to use 40,000 psi water jet. Also some chemical solvents are used along with water jet and hand-wiping.
- Environmentally safe, effective, and low cost cleaners are desired.

Background/Problem

"One Team….Relevant, Ready, Responsive, Reliable

Problem:

OBJECTIVE

- The objective of the study was to provide recommendations on the selection of commercially available, environmentally friendly cleaners for removing road tar/asphalt from Army ground vehicles.
- Develop scientific criteria for evaluating the cleaners
- Develop a laboratory method to test environmentally friendly cleaners and processes for removing road tar/asphalt.
- Provide guidance on selecting solvent systems for removing tar from metal surfaces

Tar and Asphalt

Asphalt: A brownish-black solid or semisolid mixture of bitumens obtained from native deposits or as a petroleum byproduct, used in paving, roofing, and waterproofing.

A dark bituminous substance found in natural beds and as residue from petroleum distillation; consists mainly of hydrocarbons

Tar: A dark sticky substance obtained by distilling organic matter such as coal, wood, or peat

Elemental analysis of select bitumen (Holleran et al. 2005)

Element	Weight percent otherwise as mentioned*			
	Mexican	Arkansas	Boscan (Venezuela)	California
Carbon (C)	83.77	85.78	82.9	86.77
Hydrogen H)	9.91	10.19	10.45	10.94
Nitrogen (N)	0.28	0.26	0.78	1.10
Sulfur (S)	5.25	3.41	5.43	0.99
Oxygen (O)	0.77	0.36	0.29	0.20
Vanadium (V)	180 ppm	7 ppm	1,380 ppm	4 ppm
Nickel (Ni)	22 ppm	0.4 ppm	109 ppm	6 ppm
* ppm = parts per million by weight				

Physical Properties of Asphalt

Summary of physical properties marathon petroleum asphalt.

Property	Value*
Appearance	Black-brown solid or semi-solid
Physical State	Liquid
Substance Type (Pure/ Mixture)	Mixture
Color	Black-Brown
Odor	Tar
pH	Neutral
Boiling Point/ Range (5-95%)	>700 F
Melting Point/ Range	115-199 F
Specific Gravity	0.95-1.13
Density	7.9-9.4 lbs/ gal
* Derived from the MSDS for Marathon Petroleum Asphalt.	

APPROACH

1. Develop criteria to rank commercial environmentally friendly solvent/cleaner systems for tar/asphalt removal.
2. Identify both cleaner products and methodologies.
3. Conduct laboratory coupon evaluations using select commercial products.
4. Laboratory evaluation of select solvents with field samples.
5. Develop a test protocol and a guidance document for selecting a cleaner for removal of tar/asphalt from ground vehicles.

Criteria for Solvent Selection

The following criteria were considered for selecting a solvent for removing tar from vehicle surfaces:

1. ***Effectiveness in removing the tar and fast drying***
2. ***Shall have low VOCs***
3. ***Shall have no or low content of HAPs***
4. ***Shall have low toxicity***
5. ***Shall have high flash point***
6. ***Shall have low flammability***
7. ***The ability to recycle the solvent***
8. ***The cleaner residues must be biodegradable and easily treatable along with regular wastewater streams***
9. ***Material compatibility, use of the solvent should not lead to corrosion or erosion, if possible provide corrosion protection layer***
10. ***The cost of the solvent and the solvent requirement should be minimal.***

Literature Review

Laboratory standard testing protocols available in literature for tar removal from metal surfaces were reviewed. Search was conducted on multiple databases comprising of Scopus, Academic Search Premier (Ebsco), Academic Onefile (Gale), Web of Science-including Social Sciences, Medicine, Humanities, and Engineering.

From the review of the literature it appears that the best performing solvents all have an appreciable ability to dissolve asphalt and asphalt compounds.

Both terpene-based compounds and vegetable oil esters appear to be especially favored due to their perceived environmental friendliness. The inclusion of surfactants appears to aid the process.

47 solvent cleaners were reviewed.

EXPERIMENTAL PROTOCOLS

There is no quantitative standardized procedure to compare the efficacy of these solvents.

The goal was to develop a standardized procedure that would yield quantitative and repeatable results.

Tar removal experiments were designed and conducted using commercial solvents. The solvents were tested on metal coupons simulating the metal surfaces of military tactical and transport vehicles.

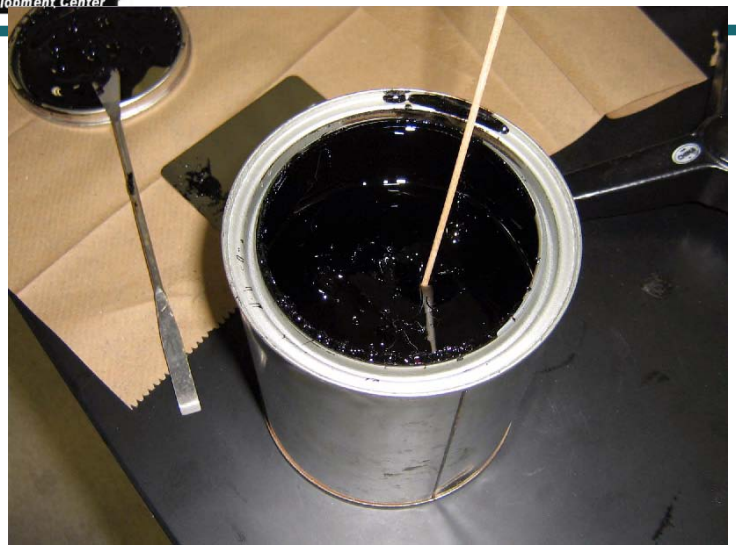
- Solubility of tar in solvents (in vials)
- Evaluation with coupons
- Evaluation of cleaning with field samples

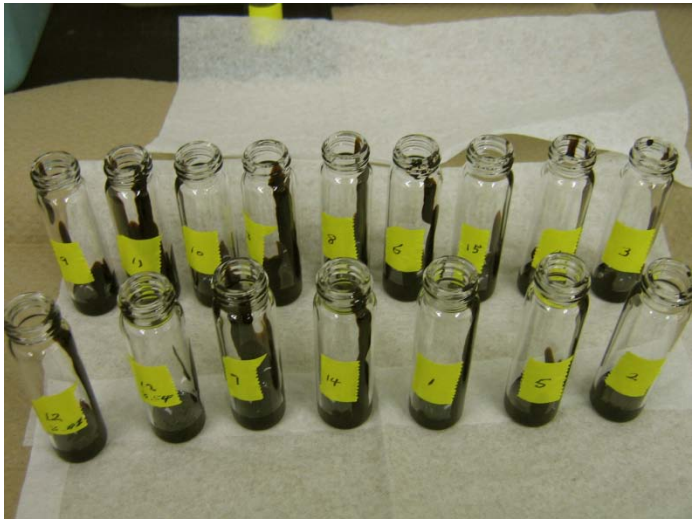
Laboratory Evaluation of Solvents

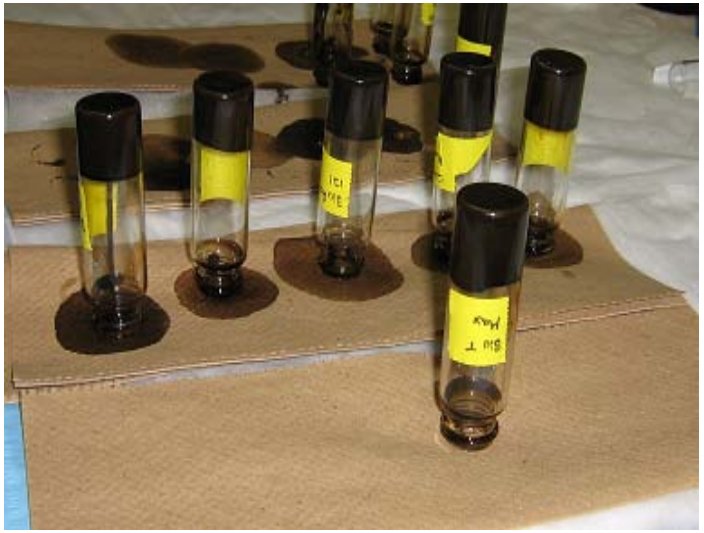
- Solubility of tar in cleaning solvents
- Coupon studies for cleaning efficiency
- Study operating parameters
  - Duration for cleaning
  - Temperature
  - Dilution
- Field samples (chains) cleaning

45 Commercial Tar Removal Solvents Are Reviewed

Tar Solubility Study







Solubility of the tar was obtained to rank the solvent systems

Chain Results

Before

After

Solubility Results

Solvent Name	Bottle Weight, (g)	Bottle Weight with tar,(g)	Tar weight (g)	Bottle weight after 5 mL solvent (g)	Amount tar removed (g)	Percent Removed	Amount of tar removed per mL solvent (g/mL)	Cost per gallon**
Citri-Zip	12.64	17.13	4.49	16.95	0.18	4.01%	0.036	$58.85
BioAct 121	12.16	16.94	4.78	16.75	0.19	3.97%	0.038	$22.40
Citrus Soy Gold	12.64	16.60	3.96	16.45	0.15	3.79%	0.03	$28.73
Bio T Max	12.61	17.52	4.91	17.35	0.17	3.46%	0.034	$25.65
BioAct 105	12.75	17.56	4.81	17.40	0.16	3.33%	0.032	$16.92
Citrus King	12.16	17.23	5.07	17.07	0.16	3.16%	0.032	$39.00
BioAct MSO	12.20	17.30	5.10	17.14	0.16	3.14%	0.032	$22.18
BioAct 120	12.61	16.88	4.27	16.75	0.13	3.04%	0.026	$24.82
Full Force	12.70	17.33	4.63	17.19	0.14	3.02%	0.028	$39.00
Tuff Stuff	12.79	17.66	4.87	17.55	0.11	2.26%	0.022	$166.00*
Orange Oil Slicker	12.68	17.56	4.88	17.45	0.11	2.25%	0.022	$26.91
DS-104	12.60	17.72	5.12	17.61	0.11	2.15%	0.022	$30.82
Rid-O-Grease	12.69	17.29	4.60	17.20	0.09	1.96%	0.018	$56.00
Citri-Kote	12.69	17.01	4.32	16.93	0.08	1.85%	0.016	$36.50

EXPERIMENTAL STUDY

- Based on the literature review of the protocols, a modified protocol as described here was followed for this experimental study.

- Preparation of Test Strips

  The assay used test strips of stainless steel with dimensions 4 in. x 6.0 in. x 1/50 in. Immersions in solvents were carried out by placing the strips in clamps and immersing two thirds of the total area of the strip. This provides a total uniform area of exposure of 12.0 sq in. The strips were desiccated and weighed with the clamp assembly so that the strip itself would not be handled.

- The asphalt used in these experiments was a standard commercially available material labeled CRS-2. The strips were dried in an oven for 24 hours at 60 °C. At the end of the drying period, the strips were cooled to room temperature and weighed. A thin edge from the bottom of the strip where lip formation was seen was removed manually.

Coupon Studies: Coupon preparation

Coupon as received

Asphalt coated coupon

Coupon preparation: Drying

Asphalt drying after coating

Solvent Evaluation

1. 

Lip at bottom.

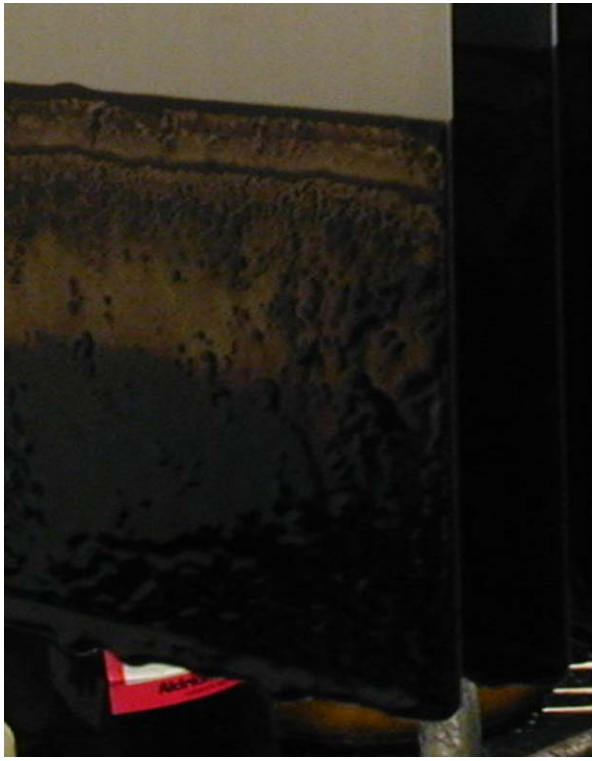
2. 

Diesel.

Solvent Evaluation

Bioclean; residue without water rinse.

1.



X-Force.

Solvent Evaluation

Bioclean coupon— ridge removed before solvent dip: Note flash rust.

X-Force.

Solvent Evaluation

Axarel 32

Bio T Max

Solvent Evaluation

Note lack of lip after modified protocol. The water rinse also helps remove residue.

DATA ANALYSIS AND INTERPRETATION

- **Table lists the raw data for the four solvents tested. Note that the residual amounts of asphalt for both diesel and Bioclean were much improved compared to the trial results. This is attributable to the elimination of the lip formation observed previously.**

Table. Raw data for the three solvents evaluated.

Solvent	Diesel	Bioclean	Diesel	BioTMax	Diesel	Axarel 32
	98.74	97.37	97.9	98.23	95.79	94.09
	98.44	99.64	97.57	97.33	94.09	94.48
	98.01	99.72	97.65	98.14		96.60
	98.16	99.58	96.52	97.89		95.53
	98.84	99.18	98.39	98.3		93.97
		99.55	97.54	97.33		97.27
Average %deviation	98.44	99.17	97.60	97.87	94.94	96.65
Std. Dev	0.36	0.91	0.61	0.44	1.20	1.36

ANOVA ANALYSIS

ANOVA analysis of test results

Groups	Count	Sum	Average	Variance		
Diesel	5	492.191	98.4382	0.129035		
Bioclean	6	595.0416	99.17359	0.8191		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	1.474919	1	1.474919	2.878427	0.124006	5.117357
Within Groups	4.611639	9	0.512404			
Total	*6.086558*	*10*				
Diesel	6	585.57	97.595	0.37747		
BioTMax	6	587.22	97.87	0.1942		
Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.226875	1	0.226875	0.793727	0.393906	4.964591
Within Groups	2.85835	10	0.285835			
Total	*3.085225*	*11*				

List of Tar Removing Solvent Systems

No.	Product	Manufacturer
1	57A Degreaser	Beaver Research Company
2	Bio T Max	BioChem Systems
3	BioPro	BioSystems, Inc.
4	Tarva-Sol Chem 243	Chemco Industries
5	Citrus Blast	CleanLine Products
6	Orange Waterless	Coastwide Laboratories
7	EcoGent Universal Cleaner	Cogent Environmental Solutions
8	R-109 Delco Red	Delco Cleaning Systems
9	C-Tar Melt	EaCoCHEM
10	Electron 296	Ecolink
11	Teksol EP	Inland Technology
12	#141 Vehicle Wash	Kleen all Plus
13	Agri-Sol	Momar
14	Vega-Sol	Momar
15	T-300 Tar Remover	Ostrem Chemical Company
16	Axarel 32	Petroferm
17	#739 Citrol II	Schaeffer Mfg. Company
18	Tar N Glue	Selden Research Limited
19	Sentinel 700	Sentinel
20	SOYSolv	SOYsolv
21	SOYSolvII	SOYsolv
22	SOYSolvII Plus	SOYsolv
23	GoldSolv	SSpenviro
24	United 399	United Labs
25	Bio Clean	Walter
26	X-Force (L-74E)	Walter

List of Commercial Solvent Systems Reviewed

Disclaimer: **ERDC-CERL or its sponsors do not promote or endorse any of the solvent cleaners or its manufacturers. Performance of individual cleaner is provided as guidance, but actual testing should be carried out by the end user.**

Summary of Tar Removing Solvent Systems

No.	Company	Solvent	* BP	* VP mmHg	* VOC g/L	* FP	Major Chemicals	Performance	Cost	Residuals/ Byproducts	Waste Disposal	toxic
1	Beaver Research 3700 W. Kilgore Rd. Portage, Michigan 49002 Toll Free: 800.544.0133 Phone: 269.382.0133 Fax: 269.382.0214 sales@beaverresearch.com	57 A	360-410° F	30 @ Room Temp.		145° F * TCC Tester	Diethanolamine (D-60) Solvent Naphtha Medium Aliphatic	Rinses freely & completely		CO & CO2	Incinerate according to fed, state, local regs.	No toxic chemicals according to reporting requirements Section 313 40 CFR Part 372
2	Biochem systems BioChem Systems 3511 N. Ohio Wichita, KS 67219 TEL: (316) 838-4739 - - (800) 777-7870 FAX: (316) 681-2168 http://www.biochemsys.com/	Bio T Max	334° F	<2	780	130° F * PMCC Tester	D-limonene	Wipe clean or rinse with water Can be diluted Hand wipe Ultrasonic tank Dip tank Conveyorized spray system Pressure sprayers	$25.65/ g	CO	Biodegradable	Non-toxic No chlorinated solvents & petroleum distillates.
3	BioSystems, Inc. P.O. 464 Fort Collins, CO 80522-0464 (800) 224-4605 info@biosystemsinc.com	BioPro	347°F	2		>122°F CC Tester	D-limonene nonionic surfacant	Insoluble in water			100% biodegradable	Non-toxic No aerosol No CFCs
4	Chemco Industries 5731 Manchester Ave. St. Louis, MO, 63110 1-800-854-4236 Fax: 314-647-1850 info@ChemcoCorp.com	Tarva Sol	349° F	25 1.4	N/A	125° F * TCC Tester	D-lemmonine	Spray on, wipe off, can be diluted with H2O	5g PA $21.60 g	CO & CO2	Biodegradable	
5	Cleanline Products, Inc. PO Box 625 Canton TX 75103 1-888-536-5185 Fax: 903-567-4600 info@cleanlineproducts.com Coastwide Labs www.coastwidelabs.com 1-800-775-3289	Citrus Blast	<300° F 212° F	as water NA		128° F * COC Tester <160° F * COC Tester	Isoparaffins Nonionic surfactant Beta-Pinene Citrus Distillate	Dissolves no scrubbing wipe away suspended particles	32oz 128 oz 55g drums 12-1qt case 4-1g case 55g drum	From Combustion: smoke, CO2, unknown organic compounds.	Biodegradable organics. Biodegradable No phosphates or petroleum products	Non toxic as far as known to Coastwide
6	Coastwide Labs www.coastwidelabs.com 1-800-775-3289	Orange Water-less	212° F	NA		<160° F * COC Tester	Nonionic surfactant Beta-Pinene Citrus Distillate	Dissolves no scrubbing wipe away suspended particles	12-1qt case 4-1g case 55g drum		Biodegradable No phosphates or petroleum products	Non toxic as far as known to Coastwide

Experimental Setup: Chains

Room Temperature (78ºF)

90ºF

Removal of asphalt on chains at 90ºF

Solvent Name	Weight	Time submerged (min)	Amount of Solvent (mL)	Weight After	Tar Removed
Citri - Zip	54.95	60	300	48.86	6.09
Bio T Max	60.27	60	300	55.66	4.61
Citrus King	55.02	60	300	48.48	6.54
BioAct MSO	50.6	60	300	47.25	3.35
Citrus Soy Gold	51.31	120	300	47.75	3.56

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Recommendations:

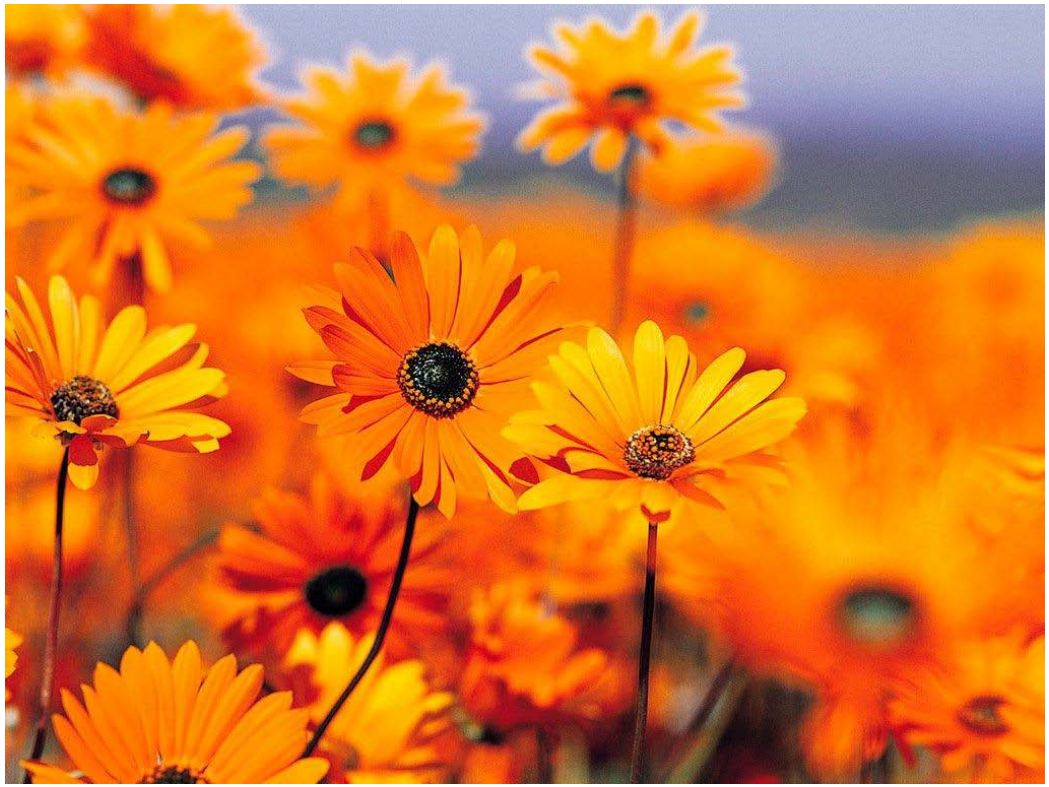
Recommendations

Solvent	Flash Point (ºF)	EPA regulated	Composition	Time (min)	Temp	Price	Producer	Phone	Percent Removed 5 mL Solvent/ Tar
Bio T Max	130	NO	D-Limonene	30-60	90ºF	$25.65	BioChem Systems	(800) 777-7870	3.46%
Citrus King	115	NO	Terpenes	30-60	90ºF	$39.00	Citrus Depot	(800) 424-8045	3.16%
BioAct MSO	117	NO	1-Methyl-4-(1-methylethenyl) -cyclohexene	30-60	90ºF	$22.18	Petroferm	(800) 367-9966	3.14%

Conclusions and Recommendation

This study revealed that at least two broad categories of solvent blends (terpene based solvents/esters, and blends of aliphatic hydrocarbons and esters assisted by surfactants) can remove asphalt from metal. However, the feasibility of using these solvents for routine large scale cleaning will have to be demonstrated in the overall framework of economics, environment, and health.

It is recommended that follow-on studies be conducted within a constraining set of environmental and health criteria and price. Given such constraints, it should be possible to formulate a custom solvent system and cleaning protocol within the constraints.



Thank you for your attention!

Questions and comments?

Project:

- Removal of tar/asphalt using environmentally friendly cleaners
- Discovering most efficient temperature
- Determining the time of dissolution for each solvent
- Analyzing the cost of each solvent